



# Applied Catalysis B: Environmental

journal homepage: [www.elsevier.com/locate/apcatb](http://www.elsevier.com/locate/apcatb)

## Review

# Application of TiO<sub>2</sub> photocatalysis for air treatment: Patents' overview

Yaron Paz\*

*Department of Chemical Engineering and the Russell-Berrie Nanotechnology Institute, Technion, Haifa, Israel*

## ARTICLE INFO

### Article history:

Available online 16 May 2010

### Keywords:

Titanium dioxide  
Air treatment  
Patents  
Photocatalysis  
Review

## ABSTRACT

A review of patents on the application of titanium dioxide photocatalysis for air treatment is presented. A comparison between water treatment and air treatment reveals that the number of scientific publications dedicated to photocatalytic air treatment is significantly lower than the number of scientific manuscripts dedicated to photocatalytic water treatment, yet the situation is reversed upon comparing relevant patents. This indicates a growing interest in the implementation of photocatalysis for air treatment purposes, which surpasses that of water treatment.

This manuscript analyzes the various patents in the area of air treatment, while differentiating between indoor air treatment and outdoor air treatment. Specific efforts were made to characterize the main challenges and achievements en-route for successful implementation, which were categorized according to mass transport, adsorption of contaminants, quantum efficiency, deactivation, and, no less important, the adherence and the long term stability of the photocatalyst.

© 2010 Elsevier B.V. All rights reserved.

## Contents

1. Introduction.....	449
2. Statistics and trends.....	449
3. Indoor air treatment .....	450
3.1. Main challenges in indoor air treatment as reflected by patents and products.....	451
3.1.1. Mass transport.....	451
3.1.2. Adsorption of contaminants.....	452
3.1.3. Contact time .....	452
3.1.4. Degradation of specific contaminants and preventing the emission of byproducts.....	453
3.1.5. Humidity effects.....	453
3.1.6. Deactivation of the photocatalyst.....	453
3.1.7. Optimizing the utilization of photons.....	454
3.1.8. Adhesion of photocatalyst to substrates .....	455
3.2. Design patents.....	456
4. Outdoor air treatment .....	457
4.1. Main challenges in outdoor treatment.....	457
4.1.1. Mass transport.....	457
4.1.2. Adsorption of contaminants.....	457
4.1.3. Deactivation of the photocatalyst .....	457
4.1.4. Optimizing the utilization of photons.....	457
4.1.5. Adhesion of photocatalyst to substrates .....	457
5. Conclusion.....	458
Acknowledgment .....	458
References .....	458

\* Tel.: +972 4 8292486; fax: +972 4 8295672.

E-mail address: [paz@tx.technion.ac.il](mailto:paz@tx.technion.ac.il).

## 1. Introduction

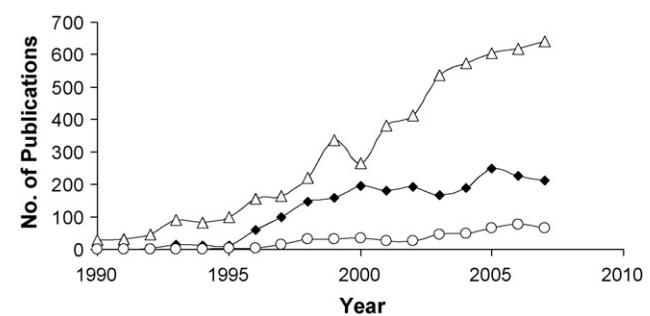
The scientific observations of the photocatalytic effects of titanium dioxide date back to years 1930–1965, where studies were performed mostly in the context of understanding the “chalking” phenomenon [1] and the degradation of colorants [2] in exterior paints. Few other works studied selected reactions [3,4] however these studies were, to large extent, sporadic and did not produce a significant scientific impact or commercial interest in the utilization of TiO<sub>2</sub> as a photoactive material.

The pioneering paper of Fujishima and Honda [5] on water splitting paved the way to thousands of manuscripts and patents aimed at the utilization of titanium dioxide for water splitting, water treatment, air purification and self-cleaning of surfaces. The first applications that were considered had to do with energy [6,7] quite coherently with the energy crisis of the mid-seventies. It took awhile until the possibility of using the photocatalytic properties of titanium dioxide for environmental purposes was realized. Once realized, the number of publications has boomed, in correlation with increasing awareness to environmental issues.

The practical use of photocatalysis seems to be by far less developed than the scientific interest. This is easily reflected by the large number of published scientific manuscripts in comparison with the small number of products that appear in the market and by the fact that until now, more than 25 years after the first “modern” manuscripts on photocatalysis, and despite the expectations, photocatalysis has not come yet to a point where it affects the daily life of the average person.

Unlike scientific manuscripts, where changes in their numbers and in the type of journals that publish them can be considered as representing scientific interest and trends, the evaluation of commercial applications is much more evasive. Yet, some feeling of the commercial situation can be inferred from analyzing products and related patents, as products and patents reflect the prospects that the commercial community assigns to a specific issue. Unfortunately, although one may find specific manuscripts aiming at specific applications, it is almost impossible to locate publications that provide analyses of the commercial situation. One of the few overviews on commercial applications of photocatalysis was published in 2002 by Mills and Lee [8]. Here, the authors used the World Wide Web to identify the major companies that promoted products that utilized semiconductor photocatalysis and analyzed their products based on the meager scientific information given in the companies' homepages. They further classified the products according to their use (air purification, water purification, sterilization, superhydrophilicity) and listed some of the patents associated with the products.

Although analyzing the self-promoting homepages of the relevant companies gives important hints regarding the commercial situation and trends, its benefits are inherently limited due to frequent changes in the content of web-pages and the fact that firms are often sold or merge thus deleting their homepages. Most important, manufacturers rarely publish any detailed information concerning their products. This is in particular true with respect to the performance of their products relative to the performance of their competitors' products and with respect to specific problems and obstacles that they had to confront during the developing of their products. The issue of comparing between products can be solved, at least partially, by standardization of efficiency-measuring methods. As for the specific problems encountered en-route for commercialization (and no less important, the obstacles that are still have to be solved) these can be deduced by analyzing the patents on which the products are based. These two issues are the core of the following manuscript, which self-limits itself, out of all applications, only to air purification.



**Fig. 1.** Estimated number of scientific manuscripts on titanium dioxide photocatalysis per year, categorized according to: water treatment (empty triangles), air treatment (filled diamonds) and self-cleaning surfaces (empty circles) [6].

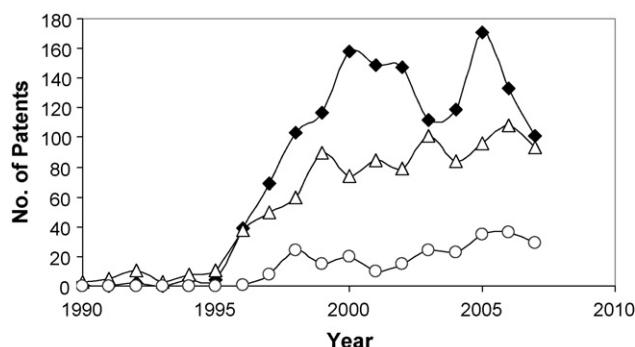
Patents differ from scientific manuscripts by the fact that they are published prior to their examination. Furthermore, many of the provisional patents are abandoned by the authors due to economical reasons. Yet, we do believe that it can be fruitful to discuss all categories without omitting any. While doing so, it is noteworthy that for the sake of simplicity we refer in the remainder of this manuscript to all these categories as “patents”. Further information on the 2009 status can be deduced by reading the appropriate reference at the end of the manuscript.

In most journals, including the present, it is customary, when referring to patents, not to mention the title of the patents in the references section. However, we do believe that in the framework of this specific review, a lot can be learned from the titles given by the inventors, as these titles usually reflect what the inventors perceived, at the time of the invention, as their main contribution. It is for this reason that the titles were included in the references section, and the reason for which the attention of the readers is drawn to this fact.

While reading over 120 patents on photocatalytic air treatment, the authors have noticed that the majority of patents, whenever citing prior art (patents and scientific manuscripts), do it in a manner that is far from being comprehensive or satisfactory. One of the few exceptions is Patent No. US 6,179,972 [9], which gives an excellent review of the patents that were relevant for its subject. Regardless of the reason for ill-citing, it is hoped that the following manuscript will not only assist the readers in understanding the obstacles for implementation and what is the current situation in overcoming these obstacles, but also serve as a platform of reference for future inventors.

## 2. Statistics and trends

The information revolution, manifested by the use of computerized search engines provides an easy way to get statistics about trends in science and technology. Fig. 1 presents the estimated number of scientific manuscripts on titanium dioxide photocatalysis per year, categorized according to: water treatment, air treatment, and self-cleaning surfaces [10]. The results presented in Fig. 1 were acquired by counting hits upon using SciFinder Scholar™ (2007) as a search engine, having “Titanium dioxide”, “Photocatalysis”, and “Air treatment”/“Water treatment”/“Self-cleaning” as keywords. As mentioned by the authors of this work, it was obvious that the total number of publications on titanium dioxide photocatalysis was larger than the sum of papers in these three categories, as these three categories cannot cover all the categories in the field. It was further clear that many of the relevant publications did not mention explicitly any medium in their abstracts. Furthermore, there is a non-zero chance that some authors used synonyms (for example, “titania” instead of “titanium dioxide”) throughout the whole abstract. Yet, the main features of the graphs,



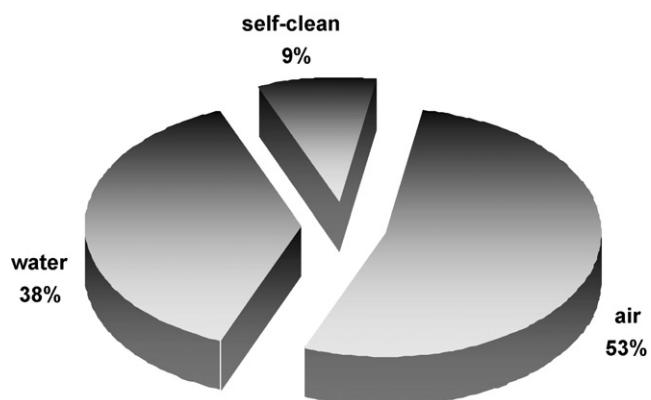
**Fig. 2.** Estimated number of patents on titanium dioxide photocatalysis per year, categorized according to: water treatment (empty triangles), air treatment (filled diamonds) and self-cleaning surfaces (empty circles) [6].

namely, the lag in the research on air treatment, the monotonically increase in the number of publications in each of the categories, and the fact that water treatment is still the subject of most of the scientific manuscripts on TiO<sub>2</sub> photocatalysis seem to be genuine.

The lag in the realization of the potential of TiO<sub>2</sub> photocatalysis for air treatment is clearly demonstrated through examination of relevant patents. The first patents on titanium dioxide photocatalysis dealt with hydrogen production (for example, a 1976 patent by Ikeda et al. [11] and a 1977 patent by Nozik [12]), quite in parallel to the use of titania as a catalyst for specific reactions (for example, two patents from 1971 and 1972 by Juillet, Teichner and Formenti on the oxidation of isobutane and other gaseous hydrocarbons to acetone [13,14], a 1978 patent by Schrauzer and Guth on the photoreduction of nitrogen [15] and a 1981 patent by Bard and Kraeutler on photocatalytic decarboxylation of saturated carboxylic acids [16]). The first patents on water treatment appeared in the beginning of the eighties. Examples include a 1979 patent by Hemmerich et al. [17] and a 1985 patent named explicitly "water purification" [18]. Patents on gas phase photocatalytic degradation began to appear in the mid eighties, demonstrating the ability to treat vaporized compounds [19] and to deodorize rooms [20,21]. It was not until 1990–1991 that the decontamination of air was explicitly mentioned in patents, for example, by Kato et al. [22], Raupp et al. [23], Watanabe et al. [24], and Aragai et al. [25]. Almost all of these patents were assigned to Japanese firms such as Fuji Electric Co. Ltd, Hitachi Ltd., Matsushita Ltd., and Toyota Ltd.

Fig. 2 presents the annual number of new patents on titanium dioxide photocatalysis categorized according to the three categories of Fig. 1 [10]. Here, again, it was not claimed that the sum of the three categories added up to the number of patents in photocatalysis, nevertheless, there is ground to assume that the ratio between the three categories is reflected in the figure. From the figure, it is evident that year 1995 was a turning point year with respect to the number of issued patents. The years 1995–2000 seem to be the "booming" years in which the annual number of patents grew fast and monotonically. Ever since year 2000, the annual number of patents remained constant more or less, probably indicating that the field enters its maturity period. The fact that as of 1997 the number of patents on air treatment surpasses that of water treatment is quite striking, especially if one takes into account that the number of scientific publications on water treatment is by far larger than that of air treatment (Fig. 1).

The large annual number of patents on photocatalytic air purification is portrayed again in Fig. 3, which presents the distribution of patents between the above-mentioned three categories on a cumulative basis [10]. Evidently, the number of patents on air treatment is larger than the sum of patents on water treatment and on self-cleaning surfaces.



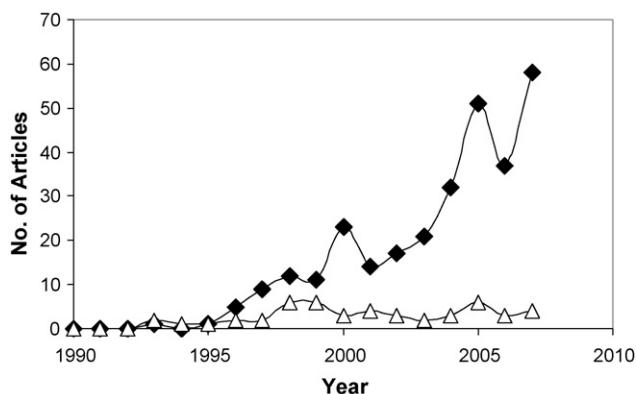
**Fig. 3.** The distribution of patents between the three major categories (air treatment, water treatment and self-cleaning) on a cumulative basis [6].

In the context of gas phase photocatalysis, it is possible to identify four major types of applications: indoor air, outdoor air, process gases, and dissolved pollutants. These four types have characteristic properties, which may affect the type of optimal photoreactor and material to be used, as well as the effectiveness of photocatalysis relative to other means of treatment. Outdoor applications and some of the indoor application are often based on large photocatalytic surfaces, which act to oxidize adsorbed molecules, thus serving a dual purpose of self-cleaning and air purification. The present review discusses air purification only.

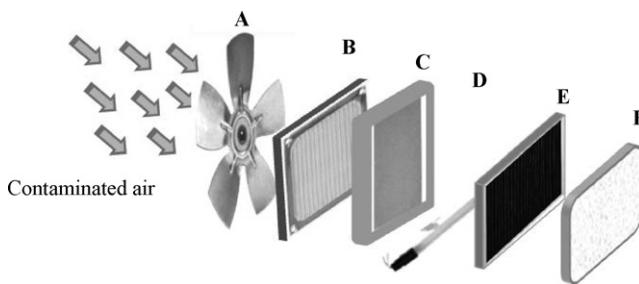
Fig. 4 presents the annual number of manuscripts dedicated to photocatalytic indoor air treatment as well as the annual number of papers dedicated to photocatalytic outdoor air treatment, as deduced from the number of SciFinder Scholar hits [10]. The figure clearly demonstrates that the scientific interest in photocatalytic indoor air treatment is by far larger than that of photocatalytic outdoor air treatment. Furthermore, the number of manuscripts on photocatalytic indoor air treatment seems to grow very fast over the last decade, in correlation with the trend of the overall number of manuscripts on photocatalytic air treatment (Fig. 1). Each type of application has its characteristics in terms of contaminant species, limiting factors and products, as described below. This overview is divided accordingly.

### 3. Indoor air treatment

An indoor air environment is basically any air-containing environment that is at least partially disconnected from outside



**Fig. 4.** Estimated number of manuscripts per year on photocatalytic indoor air treatment (filled diamonds) and on photocatalytic outdoor air treatment (empty triangles) [6].



**Fig. 5.** A schematic view of a photocatalytic indoor air treatment device. Changes may vary from product to product. (A) fan, (B) particulates (HEPA) filter, (C) photocatalyst, (D) light source, (E) activated carbon filter (optional) and (F) ionizer generator (optional).

environment, in a manner that the physical conditions prevailing are different, in terms of gas composition, pressure, or temperature from the conditions prevailing at the outside environment. For most cases, this means that the levels of pollutants in the confined places are above the ambient concentrations outside. Accordingly, this term is relevant not only to buildings, but also to underground garages, vehicles, aircrafts, storehouses and the like. Generally speaking, the indoor air environment is, at least to some extent, controllable. The control can be obtained by variety of means, some of which are very simple (opening a window, for example) whereas others can be quite sophisticated. Among these, one may outline an on-demand ventilation with pre-determined (or even dynamically controlled) humidity and temperature, triggered by the concentration of CO<sub>2</sub> in the confined place.

The variety of chemicals emitted indoors is enormous. Investigations of gaseous contaminants in buildings, including buildings that suffer from the so-called "Sick Building Syndrome" (SBS), have shown that the concentrations of individual species are in the order of 0.1 parts per million by volume (ppmv), and that the total concentration of VOCs is between 0.5 and 2.0 ppmv [26]. Among the contaminants one finds formaldehyde, acetaldehyde, aromatic compounds, hydrocarbons, NO<sub>x</sub> and CO. It is quite amazing that it took quite awhile until the diversity of contaminants in indoor air (and their implications – see Section 3.1.6) was recognized in terms of the need to perform measurements in a gas mixture, or better-under real conditions. In this context, it is noteworthy that a 1996 patent on integrating a photocatalytic device within a heating, ventilating and air-conditioning (HVAC) system for indoor air treatment mentioned throughout the whole patent only the oxidation of CO to CO<sub>2</sub> without mentioning at all the existence of other contaminants [27].

Photocatalysis seems to be well-suited for the purification of indoor air, in particular if compared with purification of water, as was analyzed by Agrios and Pichat who pointed out that the low concentrations of pollutants found in air facilitates continuous operation without saturating the surface of the photocatalyst [28]. To this, one may add the possibility of using photocatalysis for both VOCs mineralization and bacterial disinfection, upon addition of metallic (usually silver [29]) nanoparticles. Indeed, it was claimed that the market share of indoor air treatment products out of the total market of photocatalytic products grew by a factor of 3–4 between year 2002 and year 2003 [30]. At any case, the photocatalytic market is still dominated by products utilizing superhydrophilicity and by self-cleaning surfaces (some of which claim to have air purification properties).

Indoor air treatment takes place usually by using apparatuses through which air is circulated. Such systems contain a blower or an air-pump, a particulates filter or an electrostatic precipitator, a light source and a photocatalyst (see Fig. 5). It is common that the photocatalyst is fixed on a substrate, either in a honeycomb-type

construction to reduce pressure drop [31] or in a three dimensional porous structure.

Generally speaking, photocatalytic air treatment reactors can be categorized according to their geometry or according to the way by which the photocatalyst is introduced into the reactor. In terms of geometry the most common (both in scientific publications and in patents) are tubular, annular and flat plate types of reactors. In terms of the photocatalyst type and arrangement of the photocatalyst within the reactors one finds a large variety of types. Powder layer reactors and fluidized bed reactors (usually in a tubular geometry) were among the first to be used. Coated wall-parallel flow reactors and honeycomb/foam monolithic reactors are probably the most abundant products nowadays. One may also find packed bed reactors, plasma driven reactors and permeable layer reactors. The various types of reactors for photocatalytic air decontamination are reviewed elsewhere [10]. Most patents, whose subject is treatment of polluted indoor air, do not refer to a specific indoor air location, and concentrate on describing ways to achieve better performance. Nevertheless, there are several patents aiming at specific locations such as vehicles [32] and clean-room facilities [33].

Another approach for indoor air treatment uses photocatalytic surfaces such as painted walls or transparently coated windows. In that case, operation relies on natural convection, or on circulation of air by air-conditioning systems/ceiling fans. The light source in this case is either the regular light source of the indoor space (usually a fluorescent lamp with very small fraction of UV photons) or low intensity diffused solar light entering the indoor space.

### 3.1. Main challenges in indoor air treatment as reflected by patents and products

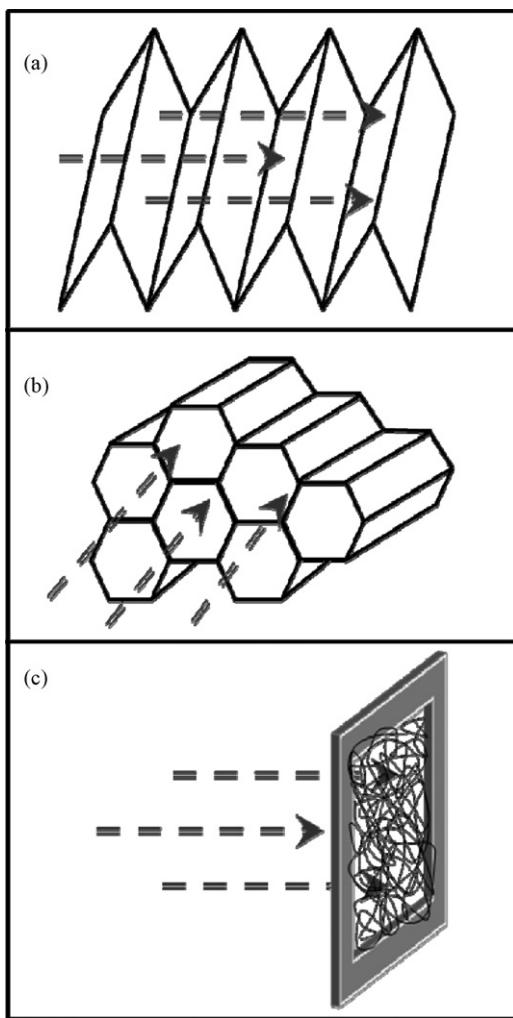
There are several challenges associated with using photocatalysis for indoor air treatment. The following section describes many of the obstacles that were faced, and are still being faced by the industry in way to achieve practical, working devices that can be sold successfully in the market. Unfortunately, reliable data on these issues is hardly available in manufacturers' bulletins or homepages. Hence, the section was written based on information gathered from patents, assuming that this type of information represents the applicative side of photocatalysis better than scientific manuscripts. The reader is advised to be aware of the fact that specific products may utilize more than only one patented concept, material or design.

#### 3.1.1. Mass transport

The transfer of the contaminants to the surface of the photocatalyst in one of the most crucial issues that have to be solved, whenever an indoor air has to be treated. The importance of this issue stems to large extent from the fact that it is usually impossible to point out one specific point source for indoor contamination. Moreover, the size of an average indoor facility, whether it is a room, hall or an underground parking lot is usually too large to rely on diffusion or on natural convection.

It is for this reason that most of the devices for photocatalytic treatment of indoor air are based on a forced flow of air, by using various types of fans that bring the contaminated air to the vicinity of the photocatalyst surface. This is reflected by a large number of patents on forced flow of air to the photocatalyst. While all these patents share the principle of forced flow, they can be still very different as for the way by which they materialize this principle.

Most of the patents on indoor air treatment utilize fixed-bed reactors, mostly coated-film reactors, although one may find also fluidized bed reactors [34]. The flow of air around the photocatalyst in coated-film reactors may take place in various configurations, as shown in Fig. 6. These configurations may include a honeycomb structure, a folded accordion structure, flow through fibrous mat,



**Fig. 6.** Typical configurations of photocatalyst in coated-film photocatalytic reactors. (a) Accordion-like film, (b) honeycomb configuration and (c) fibrous mat configuration.

and even flexible strips coated with catalyst [35]. Honeycomb structures were patented in various materials, pore length and pore size (from micrometer-size pores, up to several centimeters [36]). Here, since the light source is located in front of the honeycomb, care has to be made to properly design the size of the honeycomb (lateral versus depth dimensions) to ensure that all coated surfaces get the required illumination.

An interesting way, remarkable in its simplicity, to assure airflow towards the photocatalyst is to attach the photocatalyst directly to the surface of the blades of a fan [37,38]. At first glance, this design seems to solve the mass transport problem at almost no cost, nevertheless, a second examination reveals that this design inherently limits the working surface to the area of the blades. Another obstacle is the high shear rate that the surface of the blades experience. While this shear rate is not expected to harm a well-adhered film comprised of sintered nanoparticles, it is definitively a problem whenever a (more efficient) film made of larger particles (such as Degussa P25) is used.

Solving the mass transport problem is easier when the contamination arrives from a point source. In this case, it is preferable to introduce the photocatalyst as close as possible to the source. Such an example is given in a 1997 patent, whose subject is the coating of furniture and other formaldehyde-emitting wooden articles with TiO<sub>2</sub> [39]. According to this patent, the photocatalyst is fixated to the surface by a roller pressed acrylic or silicone film. It is notewor-

thy that in this patent the effect of silicones on the photocatalytic activity (see below) and on the concentration of oxygen are not discussed. Another example is a multifunction peripheral device (scanner) that contains a built-in photocatalytic device [40]. Such a solution spares the need for overall circulation of all the air body in the facility, thus reducing the size and the energy demands of the photocatalytic device. Furthermore, it can be coupled in a manner that operates only when the contaminating device is turned on.

Still, there are quite a few patents for indoor air treatment that do not utilize integrated forced air devices. These include screens, painted walls, coated lamps and other articles that might be indoors, all relying on the circulation of air by opened windows, ceiling fans or air-conditioning systems. Taken the low UV intensity that the photocatalyst is exposed to, it is not clear to what extent these patents are indeed materialized in the form of operating market products for air cleaning.

### 3.1.2. Adsorption of contaminants

The adsorption of the contaminants on the surface of the photocatalyst is an important factor for achieving high degradation rates. Unlike the aqueous phase, where one may change the pH of the solution to control surface charge hence to promote adsorption of charged species, controlling the adsorption of gas phase contaminants seems to be more complex. Still, altering the acidity of the surface of titanium dioxide (for example, [41] by a monomolecular layer of tungsten oxide having a surface pH of 1.7) was proposed as a means to improve adsorption, and accordingly to improve efficiency.

Adsorption can be increased by using composite structures that are comprised of inert, adsorptive domains, co-existing with photocatalytic domains. Here, in the so-called “Adsorb and Shuttle” (A&S) effect [42], the contaminants are first adsorbed on the inert sites and then diffuse to the photocatalytic domains. It is noteworthy that the first patents utilizing the “Adsorb and Shuttle” approach considered the photocatalytic part as a means to regenerate an adsorbent (usually activated carbon [43]). It took awhile until the focus has changed from regeneration of adsorbents to adsorption-assisted photocatalysis. One example for the A&S approach is a patent consisting of plurality of hairlike textures, made from synthetic fibers, onto which a layer of a mixing agent (containing an antistatic agent and a dispersant), a layer of a crosslinking agent and an outer photocatalyst layer were coated [44]. Another example is a composite photocatalyst comprising of carbon nanotubes (CNTs) and titanium dioxide, where the effect of the CNTs is both electronic and adsorptive [45]. Likewise, to increase the adsorption of low polarity organic compounds it was proposed to utilize the increased affinity between these molecules and platinum. Here, the concept was to use a thin overlayer of porous titanium dioxide coated on an underlayer comprised of platinum and titanium dioxide [31].

High concentration of contaminants that temporarily exceeds the maximal concentration that can be handled by a specific photocatalytic device can be handled by coupling the photocatalytic device to an adsorption module that temporarily retains a portion of the contaminants in the gas stream [46]. The operation is based on releasing the adsorbed contaminants, thus regenerating the adsorption module, as soon as the concentration of contaminants in the gas is below a pre-designed threshold.

### 3.1.3. Contact time

Assuring operation at an optimal contact time (in the context of photocatalysis contact time is the time that the gas molecules are in the irradiated, operating area) is very difficult to achieve in a pre-designed apparatus, simply because the concentration of contaminants varies from place to place and as a function of time. One

way to control the contact time is to set the photocatalytic unit at a bypass to the main air flow stream. A movable baffle is then used to divide the air flow between the bypass and the main stream, thus controlling, in practice, the time that the contaminated air is under irradiation [47].

### 3.1.4. Degradation of specific contaminants and preventing the emission of byproducts

A survey of the patent literature from the early days of photocatalysis reveals several patents whose subject was the use of photocatalytic processes for the degradation of specific compounds. The core of these early days patents was the use of photocatalysis for solving a specific problem with a specific target molecule rather than disclosing an innovative design aimed at making the photocatalyst specifically suitable for the target compound. Since at the time of application there was already scientific literature on the photocatalytic degradation of these molecules in the context of air treatment, it is not clear to what extent these patents are challenge-proof.

In the last decade a different, more advanced, class of patents describing designs especially developed for handling specific target molecules was disclosed. One of such polluting agents is ozone that is inefficiently decomposed by titanium dioxide. To overcome this problem, it was proposed to combine photocatalysis and thermocatalysis in one device, for example, by using a layer consisting of titanium dioxide and manganese oxide [48]. In a follow-up patent [31], the coating included an inner layer comprised of manganese oxide (alternatively Pt and Au) and titanium oxide and an outer layer made of titanium dioxide. The outer layer was thin and porous. Its task was to oxidize volatile organic compounds, while the task of the inner layer was to decompose ozone to molecular oxygen utilizing the effectiveness of manganese oxide as a room temperature thermocatalyst. The same concept was demonstrated, in the same patent, in the oxidation of carbon monoxide by an inner layer made of gold/titania.

A sub-topic of treating specific contaminants is the prevention of emission of specific byproducts formed during photocatalytic air treatment. One of the most important examples is preventing the emission of phosgene, which is a byproduct of the gas phase photocatalytic degradation of trichloroethylene (TCE) [49]. Here, a patent issued in 2002 coupled between particles of metals such as copper, zinc, iron, tungsten, molybdenum, and chromium, acting as catalysts for phosgene, and a photocatalytic substrate made of titanium dioxide [50]. In one of the examples, given in the patent, a comparison was given between using titania and metal-loaded titania. At an inlet TCE concentration of 200 ppm, both photocatalysts converted 91% of the TCE. Yet, the phosgene concentration in the outlet effluent was 3.5 ppm with titanium dioxide and no more than 0.25 ppm with a photocatalyst impregnated with copper–molybdenum.

Combining photocatalysis and thermocatalysis at elevated temperatures (300–600 °C) was claimed to increase the yield of CO<sub>2</sub> from TCE after 120 min of exposure, from 26% to 77% [51]. Likewise, the amount of released byproducts was claimed to be reduced in a two steps device, where the first, photocatalytic step is followed by a second, catalytic step [52]. That way, the long residence time that is often required to achieve complete mineralization was no longer needed. The inventors provided in their patent two classes of thermal catalysts, optimized for two classes of contaminants: halogens-containing contaminants and contaminants that do not contain halogens. The same concept of combining photocatalysis with thermal catalysis was implemented within a single coating aimed at oxidizing carbon monoxide to carbon dioxide [53]. Here, gold nanodomains (smaller than 3 nanometers) served to lower the energy barrier in the oxidation of CO to CO<sub>2</sub>.

### 3.1.5. Humidity effects

Water molecules participate in the photocatalytic process both as competitive adsorbents, OH sources and reaction products. Hence, it is obvious that variations in the relative humidity may have a significant effect on the photocatalytic efficiency and in certain cases (trichloroethylene, for example, [54]) even on the chemical mechanism of degradation. Unfortunately, air purifying systems may operate in an environment whose humidity might be uncontrolled. This limits the possibility of setting appropriate predictions on the performance of the photocatalytic air purifying devices. To reduce the sensitivity of photocatalytic devices to variations in humidity it was proposed to coat the titanium dioxide photocatalyst with a monolayer of tungsten oxide [55,56]. This layer was found to have a significant effect on reducing the dependence on humidity in the photocatalytic degradation of propanol and toluene (but not of butane).

### 3.1.6. Deactivation of the photocatalyst

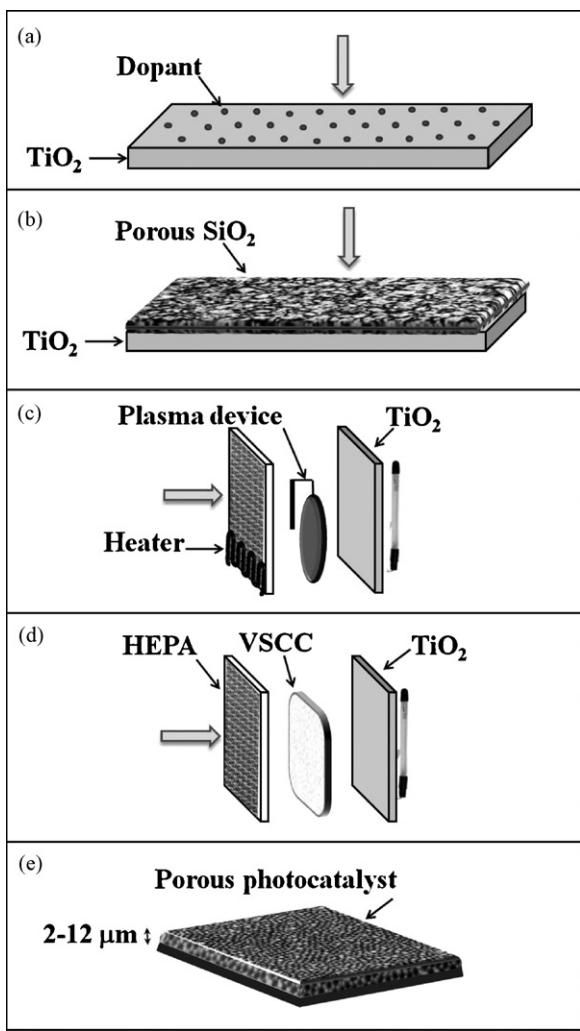
Deactivation of the photocatalyst is among the most severe practical problems, and its importance is reflected by the large number of patents claiming to solve it. It is noteworthy that this crucial problem is hardly encountered by researchers from the academia, who prefer to invest their efforts in increasing the quantum efficiency and in overcoming mass transport obstacles rather than fighting against deactivation. This difference in attitude is partially explained by the fact that the real conditions that have to be faced by the photocatalytic products are much more complicated than the relatively “clean” model systems that are traditionally studied in the academia. The long time that it takes for deactivation to appear and the tradition of performing accelerated tests in industry (but less in academia) adds to the former explanation.

Among the deactivating pollutants one may mention benzene and other aromatic compounds, Trichloroethylene, and, probably most important, volatile silicon-containing compounds (VSCCs) that become more and more abundant indoors due to their presence in the formulations of room temperature vulcanizing silicone sealants (RTV), and in cleaners, personal deodorants and shampoos. The typical indoor concentration of VSCC is typically 0.01 ppm by volume, some two orders of magnitude lower than that of VOCs, whose total concentration is typically on the order of 1 ppm [57].

It is quite amazing that the problem of deactivation by VSCCs was realized only a few years ago, when companies went into in situ indoors field-tests instead of laboratory tests. Prior to that time, developers performed laboratory tests based on testing the photocatalytic degradation of the main indoor pollutants (such as formaldehyde and BTEX) and did not consider the presence of low level of less obnoxious compounds that still have a major impact on the performance of the photocatalyst.

There are several patented ways to fight deactivation by siloxane compounds. One of these ways is based on introducing 1%-3% of dopants claimed to repel silicon compounds (Fig. 7a), and by covering the photocatalyst by a layer of hydrogen atoms claimed to eliminate or at least to reduce the forces that attract the silicon compounds to the photocatalyst. Alternatively, doping the titanium dioxide crystals was suggested as a means to prevent siloxanes' adsorption on the photocatalytic sites. According to the inventors, this aim can be achieved either by doping with dopants that repel siloxanes (such as elements belonging to groups 1, 2, 11, 12 and 13) or by introducing low concentrations of dopants that attract siloxanes (such as elements belonging to groups 5, 6, 7, 8, 9, 10, 14, 16 and 17). In the latter case, the inventors claimed that the siloxane compounds are attracted and adsorbed only onto the doped areas, leaving the photocatalyst region free to release hydroxyl radicals [58].

Other patents suggest a two layer structure, made of a photocatalytic layer, covered with a UV transparent porous protective



**Fig. 7.** Various ways to fight deactivation by VSCCs. (a) Doping, (b) two layer structure containing porous silica, (c) upstream degradation followed by deposition, (d) upstream filtration and (e) use of porous photocatalyst.

layer made of interconnected silica nanoparticles [59]. According to these patents (Fig. 7b), the tortuous pores of the overlayer facilitate the transfer of the small VOC molecules while limit the diffusion of larger molecules such as hexamethyldisiloxane (HMDS). The applicants claimed that the lifetime of the photocatalyst was expected to be doubled.

Another approach to fight deactivation caused by VSCCs is by designing a system that oxidizes the VSCCs before they reach the photocatalyst. One way to achieve it is to work with a two mode system that contains an adsorbing filter, a heating source that can heat the filter, a plasma device, a photocatalyst and a UV source (Fig. 7c) [60]. During operation in the first mode, the VSCCs are adsorbed on the filter, the heater and plasma source are off and the UV photocatalytic system are on. At a certain time the system switches to the second mode, where the UV is turned off and the heater heats the filter, desorbing the pre-adsorbed VSCCs. At the same time the plasma source is turned on thus oxidizing the emitted VSCCs to silicon oxides that are deposited on a biased electrode of the plasma device.

A very simple solution to the silicone compounds problem was suggested this year by Carrier Corporation, namely the use of an upstream VSCC filter, following the particulates-removing HEPA prefilter prior to the entrance to the photocatalytic compartment (Fig. 7d) [61]. The VSCC filter is especially designed to enhance the

removal of the target molecules by virtue of acidic sites on its surface, and by facilitating preferential interaction between the surface and the VSCC molecules. This is done, for example, by impregnating the filter in sulfuric acid or in any compound containing a sulfonic acid group. Incorporating catalytic nanoparticles of platinum, rhodium, rhenium or palladium may further serve to promote the degradation of the VSCCs. The VSCC filter may contain additives that easily form a network with silicon and oxygen, such as iron. It is noteworthy that no quantitative data on the performance of this solution was given in the application, which facilitates a comparison with the previous patents.

Another means to fight VSCC deactivation is by using a photocatalyst made of a porous skeleton [62] that is made by templating with polymers or surfactants [57]. Here, a relatively thick layer of photocatalyst (2–12 μm in thickness, compared with less than 1 μm needed for a dense film), containing pores with diameter larger than 4–6 nm was used (Fig. 7e). The large diameter of the pores was needed in order not to block the penetration of VOC molecules by the slow coverage of the pores by silicon oxide compounds formed during the degradation of VSCCs. One of the most impressive measurements presented in the patent was a linear decreasing correlation between deactivation rate and the surface area originated from pores whose diameter was larger than 4 nm. Here, a remarkable (factor 10) decrease in the deactivation rate, between a film made of P25 particles (15 m<sup>2</sup>/g of area originated from pores larger than 4 nm) and a templated film having 120 m<sup>2</sup>/g of pores larger than 4 nm was reported.

Loading photocatalysts with metals (such as silver, copper, platinum or nickel) is often used as a means to improve charge separation and to introduce antibacterial properties [63] (the latter properties are beyond the scope of this review). Loading titanium dioxide with noble metals may assist also in overcoming deactivation, most likely through the activity of the metals as thermal catalysts [64]. Usually, the metal is loaded on the photocatalyst by impregnation, either prior to coating of the photocatalyst on the substrate [65], or following its coating [66–68]. Recently, a patent on manufacturing photocatalytic air-filter loaded with metals by a photodeposition process was filed [69]. It is quite interesting that this patent did not mention as prior art the publications made by Bard et al. on the photodeposition of gold and platinum on titanium dioxide [70], which was patented already in 1980 [71]. Of interest is also a method of attaching nanoparticles of titanium dioxide onto metallic deposits having a dendritic structure [72].

Another patent that comprises metals in order to fight deactivation uses Pt-family metallic clusters for converting sulfur compounds such as SO<sub>x</sub> and H<sub>2</sub>S that tend to poison the photocatalyst to the less poisonous sulfate [73]. A side benefit mentioned in the patent is the ability to oxidize CO to CO<sub>2</sub>.

### 3.1.7. Optimizing the utilization of photons

Patents on optimizing the effects of photons can be grossly divided into two classes: patents disclosing ways to increase the efficiency by which absorbed photons are converted into charge carriers and patents disclosing ways to decrease the number of photons that are not utilized either because they are not absorbed by the surface or because they do not reach the photocatalyst surface.

Increasing the efficiency by which photons are converted to charge carriers is closely connected with efficient prevention of electron–hole recombination. The main mechanism for preventing recombination is simply the presence of adsorbed oxygen, which is present anyhow in air-decontamination units. A second mechanism to improve charge separation is comprised of electron sinks located in close proximity to the photocatalyst. Such electron sinks can be, for example, domains of noble metals (Pt, Pd and Au) [71] or even carbon nanotubes [45].

Recombination is a second order process with respect to charge concentration, as it depends on the concentration of both charge carriers. In contrast, formation of hydroxyls is a first order process. As a consequence, (above a certain flux) the quantum efficiency decreases as the photon flux is increased. Accordingly, reducing the photon flux by dividing the photon flow onto a larger area may enhance photocatalytic activity. Using plurality of glass media coated with (reflecting) TiO<sub>2</sub> is one method to achieve it [74].

In the last decade a growing number of patents describe ways to shift the photocatalytic activity towards longer wavelengths, thus increasing the percentage of solar photons that are utilized. This was usually done by incorporating nitrogen [75,76], carbon [77], or sulfur [78]. The dopant ions were claimed to be located either at oxygen sites, interstitial sites, or at the grain boundaries of the titanium dioxide particles. It is noteworthy that some of the patents on spectral shifting presented a significant shift in the absorption spectrum while claiming, without proper evidence, for improved photocatalytic activity, wrongly assuming that the larger the shift was, the more visible light active was the photocatalyst. Another characteristic of these patents (and many of the scientific publications as well) was the presentation of the activity not in terms of quantum efficiency, but rather by comparing it to the activity of titanium dioxide under the same conditions (i.e. under visible light), which is almost nil.

There are several patents on improving the performance of doped photocatalysts. One patent limited the presence of dopants, such as carbon, to the surface of the photocatalyst's particles [79]. Another patent claimed that high level of added nitrogen atoms in the bulk, to the extent that titanium oxynitrides (TiO<sub>n-x</sub>N<sub>x</sub>) were formed performed better in terms of visible light activity [80]. Such a photocatalyst, disclosed the patent, could be formed by a liquid phase reaction between an organotitanate compound dissolved in polar solvent and ammonia.

A patent on an air purifying device operating by both visible light and UV light was granted in 2006 [81]. The patent utilized photosensitizers belonging to the family of ruthenium pyridine complexes, similar to those used by Gratzel et al. in their dye sensitized solar cells (DSSCs) [82], as well as artificial and natural cyanines (for example, those found in blackberry extract). It is noteworthy that the long term stability of the photosensitizers seems questionable in our eyes, so far as they are exposed not only to visible light but also to UV irradiation.

Light sources being used in photocatalytic apparatuses for indoor air decontamination utilize artificial light. Almost all patents and products mention the use of commercially available UV-A or UV-C light sources. The quantum efficiency of doped titania under visible light is by far lower than the quantum efficiency of undoped titania under UV light. As a consequence, the gain that can be achieved by using doped photocatalysts in indoor air treatment apparatuses is very modest, especially if one considers the fact that the intensity of visible photons emitted together with the UV photons is not very high. A way to gain photocatalytic activity with visible light while maintaining activity under ultraviolet light is to combine between two types of particles. For example, a 2003 patent described a film made from fine particles of anatase bound to the substrate and to bigger particles of a visible light activated photocatalyst (rutile or nitrogen-doped anatase) by ultrafine particles of an oxide binder [83]. In our view, using doped titanium dioxide for indoor air treatment has the most prospects in those cases where the photocatalyst is coated on large area surfaces (walls, ceiling, floor or windows), such that the light source for photocatalysis is the regular visible light source used for lighting up the confined space, either artificial or natural scattered solar light.

As mentioned before, most sources in apparatuses use 254–365 nm light. Nevertheless, there are a few patents that mention lamps with shorter wavelengths, for example, a 185 nm light

source that is used for dual operation, namely generating ozone by direct photolysis of air, claimed to work synergistically with hydroxyl radicals and superoxide ions that are formed on the surface of the photocatalyst [84].

Several patents presented ways to achieve short distance between the lamps and the photocatalyst. One possibility was coating the photocatalyst on the exterior part of UV-fluorescent lamps [85], or the preparation of a glass fiber sleeve impregnated with nanoparticulate titanium dioxide and doped with N, P, or S to be wrapped around a visible light fluorescent lamp [86]. Here, the inventor did not provide any data from which one could get an impression that the invention indeed might work in actual rooms that are considerably bigger than the 5 l closed chambers mentioned in the patent. Another lamp-coated design utilizes a fan, around which a circular lamp, over-coated with titanium dioxide is mounted [87].

The UV light can be introduced by using fiber optics, whether coated with the photocatalyst or not. Some patents present claims regarding the principle of using fiber optics, despite the fact that fiber optics are reported in the scientific literature as being used in photocatalysis since the infancy of the field [88]. In the first patents [89,90] the photocatalyst was coated on the optical fibers by impregnation, followed by drying and heat treatment. Later on, a better-adhered coating, prepared by thermal hydrolysis and sol-gel process was suggested [91]. This process, which is quite common in the preparation of transparent thin films made of nanosized crystals, is known to have superb qualities in terms of adhesion to substrate and less favorable qualities in terms of photoefficiency.

One of the disadvantages of a photocatalytic air purifier that contains an artificial UV source is the danger of exposing human beings to unacceptable levels of UV radiation. Several patents were issued on structures that prevent the emitting of UV radiation generated within the devices. Apart from the trivial solution of using mechanical barriers, it was proposed to use screens with luminescent materials to convert any UV-B/UV-C irradiation that is not utilized by the photocatalytic devices into harmless visible light [92].

Reflectors, engulfing annular reactors that contain the lamps at their centers are quite common and appeared already in the early scientific publications on photocatalysis. Nevertheless, one still finds patents presenting claims about such designs.

### 3.1.8. Adhesion of photocatalyst to substrates

The adhesion of the photocatalytic material to its substrate is not one of the most studied issues in the scientific literature. Yet, when products are required to last for several years the issue of adhesion gets the importance it deserves. Good binding between the photocatalyst and the substrate is not trivial, since any organic binders might be prone to photocatalytic degradation. Many patents use simple impregnation [93] onto porous substrates or fibrous skeletons (made of oxides, polymers, metals or even paper) as a means of fixating the photocatalyst to its substrate. Alas, over time, the adherence of the photocatalyst tends to deteriorate, unless measures of prevention are taken.

One approach is to construct the film without any binder. Here, adhered films of titanium dioxide can be produced on oxide substrates by using an organotitanate precursor that forms very robust nanocrystalline films by a sol-gel process, followed by heat treatment at elevated temperatures [94]. The main drawback of this method is the relatively low surface area that is obtained, which makes the film more suitable for self-cleaning purposes than for air decontamination. Similar coating can be obtained by spray pyrolysis, chemical vapor deposition or sputtering [95]. Another patent claimed to get a hard and well-adhered coated layer without any binder simply by using a mixture made of spherical nanoparticles of titanium dioxide together with photocatalytic nanoparticles having

high aspect ratio [96]. It is noteworthy that in the examples' part of the patent, the inventors reported on a short heat treatment step at elevated temperature, which is similar to the one reported above. Another way for better adhesion of the photocatalyst is to use rapid heating [97], or supporting the photocatalyst on an electro-deposit metal, preferably of a dendritic structure [72].

A simple way to obtain a TiO<sub>2</sub> layer of superb adhesion to the substrate is to use titanium metal, while relying on the native oxide that is formed [98]. The problem is that the quantum efficiency is not expected to be very high since part of the formed titania is likely to be amorphous, not to mention the low surface area.

Organic-silane polymers (silicones), forming inorganic bonds, were suggested as TiO<sub>2</sub> binders [99]. Although the organic residues are prone to be attacked by photo-generated oxidizing species, it was claimed that the binding do not interfere with the chemical reactivity of the photocatalyst since the backbones of these polymers do not contain oxidizable atoms. It is noteworthy that silicones and silicone residues were mentioned before as deactivating agents. It is therefore quite interesting that the cited-above patent claimed that if the coverage of the silicone-residues was kept partial, there would be no decrease in the photoactivity of the photocatalyst. Similar binder appeared in a patent granted seven years later [100] on attaching titanium dioxide to wood.

An interesting approach is to use an organic polymer containing hydroxyl, ketone or carboxyl groups that interact with the photocatalyst. For example, a 2006 patent disclosed the preparation of polymer – TiO<sub>2</sub> crystals and films by a procedure comprising of hydrolysis to get titanium hydroxide, peptization with nitric acid, addition of poly(ethylene glycol), microwave treatment, drying and calcining [101]. Another possibility, similar to the previous, is to pre-mix the resin with the particles of the photocatalyst [102]. Once mixed, the mixture is electrostatically positively charged in a spray gun and carried by low velocity air to a negatively charged surface. The electrostatic charge holds the powder particles while the substrate is heated, thus burning off the resin and forming a stable, well-adhered titania film. The patent also presented methods for treating the surface of substrates, for example, phosphate treatment of aluminum, aimed at further improving of the binding.

Another way to get well-adhered photocatalytic film is by adding a few percents of an acetone-based fast-dry adhesive to an aqueous solution containing 30% by weight of titanium dioxide. The obtained colloidal solution can be applied to the substrates by spraying [103]. According to the patent, care has to be taken to regulate the weight ratio between the photocatalyst and the water, according to the exact temperature of the substrate surface. Here, again, the long term stability under UV light far from being clear.

Various manufacturers sell nanoparticulate colloidal solutions to be applied directly on surfaces by spraying and claim that the coating has superb adherence to the substrates even without any binder or the use of thermal treatment. In certain cases an undisclosed adhesion promoter layer may be required. Unfortunately, no quantitative information could be obtained regarding scratching, peeling or adherence tests in the documents published by almost all manufacturers. Several (unpublished) tests performed by us on a variety of competitive products indicate that, generally speaking, the adhesion obtained by the current products might be insufficient for long term working under weathering conditions.

Photocatalytic air treatment by fluidized bed reactors can be quite problematic if one tries to fluidize very small particles (such as Degussa P25), as the particles might be drifted away during operation. Therefore, it is often suggested to fluidize larger particles onto which the photocatalyst is attached. In that case, attrition is a major point of concern. To overcome attrition it was proposed to use composite particles comprising of a mixture of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, whose size distribution is narrow enough to make them suitable for fluidized bed reactors [34].

### 3.2. Design patents

Some patents described specific devices rather than means to achieve improved photocatalytic activity. For most cases, such patents were submitted quite awhile after the submission of the corresponding patents on new materials or processes. In principle, the claims in these patents could be expected to be much narrower than the claims disclosing new materials or processes. However, in reality, these patents often contain very broad claims that can easily be challenged. It is very common to find in the background part of the these patents a reasoning for using photocatalysis per se, without proper referring to relevant, more specific, previous art, whether patented, published or regarded to be common knowledge among skilled professionals in the field.

Most photocatalytic indoor air treatment systems are manufactured and sold as stand-alone units, nevertheless there are quite a few patents which present integrated devices, where the photocatalytic unit is included within a larger device, whose primary task can be different than air purification. Many patents described the integration of a photocatalytic device within a heating, ventilating and air-conditioning (HVAC) apparatuses. For example, a heating and cooling system that includes a combination of blower, hot air furnace and an air-conditioning unit, and had a particulates-removing filter and a purification unit at the upstream side of the blower [104]. In another example the light source was located between a honeycomb photocatalytic structure and the evaporating coils of the HVAC system, in a manner that the same UV lamps were not only used for photocatalytic treatment of VOCs in the air, but also acted as germicidal sources that handle bacteria that tend to grow on the outer side of the evaporating coils [105].

Various design patents described ways to ease the installation of a photocatalytic device within a HVAC system and the replacement of consumable parts such as filters, photocatalyst beds or light sources. A typical design belonging to this category was a device that all its parts (light source, filters, photocatalyst, etc.) were connected to a mounting body that could easily be mounted at the sidewall of an air condition duct [106]. Another design presented a modular configuration with a retractable alignment mechanism that was configured to move a modular enclosure between an in-use position and a retracted position [107]. Similarly, a recently published patent on a configuration especially designed for easy mounting into an air handling duct disclosed a planar surface for removable connection to an ultraviolet illumination device [108].

Among the specific designs of photocatalytic devices embedded within larger systems one may find a device that is directly connected to a computer, thus utilizing the same fan for cooling the computer and for drawing the air to the purifying unit [109] and a device that is connected to computer's peripheral equipment (a scanner, for example) [40]. Other specific designs include a design where a set of curved base-plates coated with a photocatalyst are located parallel to each other and have a lamp insertion hole at their center [29], or a design containing an upstream electrostatic precipitation prefilter and a heat-regenerated adsorption media located downstream to a photocatalyst-coated porous substrate [110].

A 1997 patent disclosed a device especially designed for removing NOx from vehicles [32]. Here, the inventors assumed that the observed decrease in the activity of the photocatalyst was due to reversible adsorption of end-products. Hence, they suggested to desorb the adsorbed end-products by periodically modulating the temperature of the photocatalyst (by increasing the UV light intensity or, alternatively by reducing the air flow through the device), while assuring that the emitted gas is not released into the cabin of the car. Another relevant patent for the automobile industry was an air purifying filter presented in 1998 by Fujishima, Hashimoto, Moroto, Ando and Sakai, which was designed especially to combat poisoning compounds emitted by vehicles [73].

## 4. Outdoor air treatment

The basic concept in outdoor air treatment is to use large area construction objects as platforms for air decontamination. Such platforms can be, for example, walls, roofs, roads, pavements, bridges and buildings. There are quite a few patents on the photocatalytic treatment of outdoor air. These patents are closely related to scientific work, claiming that roads painted with titanium dioxide or the use of buildings covered with cementitious materials that contain TiO<sub>2</sub> may improve the quality of ambient air [111,112]. Photocatalysis can be specifically adequate for outdoor treatment of NO<sub>x</sub>, emitted at large by vehicles, as the nitric acid formed during the photocatalytic oxidation can be washed away by rain. It is noteworthy that due to mass transport limitations (the need for the pollutants to reach the photocatalyst surface), practical use of photocatalysis for air decontamination is expected to be restricted to semi-confined places such as canyon streets, as was justly pointed out by Agrios and Pichat [28].

The photocatalyst can be applied in various forms including cementitious modules (blocks), in situ made concrete objects and over-coated thin layers (whether made of clear nanocrystalline solution or from opaque, paint-like solution). Quite often, these types of coatings are referred as “self-cleaning coatings”, since photocatalytic coatings on construction materials act to prevent also the adsorption of soot or dust that tend to stick to grimy surfaces. Although titania-coated surfaces can serve, in principle, for the dual purpose of self-cleaning and outdoor air treatment, optimization for one type of application, do not necessarily coincides with optimization for the second type of application. For example, to achieve good self-cleaning properties low specific surface area, which limits sticking, is desired, while for air decontamination a high specific surface area is preferable.

Outdoor air treatment differs from indoor air treatment by the type of contaminants (less VOCs and more NO<sub>x</sub>, CO, SO<sub>x</sub>), by the use of solar light as the dominant irradiation source, by the fact that the primary task of the photocatalytic platforms is to serve for construction (unlike indoor-air treatment devices that are especially constructed and designed for air cleaning), by the exposure to a harsh environment (temperature and humidity variations, rain, snow, shear forces) and, no less important, by their visibility to the general public. The fact that outdoor air is regarded as “public domain” and (unlike drinking water) is not regarded as a commercial product by both public and legislators has also its consequences, in terms of responsibility and regulation, which to these days are still an unsettled issue in many countries. Indeed, commercialization of outdoor air treatment is currently by far less developed than commercialization of indoor air treatment. In almost all cases where photocatalytic surfaces are used outdoors, the main aim is self-cleaning (i.e. the maintenance of private property) or, at most, demonstrative. While this lack of commercial interest of the end-consumers seems prohibitive at present, it can still be changed in future once fundamental technological obstacles are solved and the awareness among legislators and administrators is increased.

### 4.1. Main challenges in outdoor treatment

Many of the basic challenges facing treatment of outdoor air are common to indoor air treatment. Nevertheless, in light of the specific conditions under which outdoor air treatment operates, there is a need to analyze those aspects that are different.

#### 4.1.1. Mass transport

Outdoor air treatment cannot rely on artificial means like blowers or fans that will bring the contaminants to the photocatalytic surfaces. Accordingly, effective mass transport depends on

recording and understanding the environmental conditions (wind, concentration and type of contaminants) prevailing at the site. An exception is the treatment of contaminated air in tunnels, which shares some characteristics of outdoor air decontamination (NO<sub>x</sub> as the main contaminant) and some of the indoor air decontamination (semi-confinement).

#### 4.1.2. Adsorption of contaminants

One of the first patents on utilizing TiO<sub>2</sub> for the removal of NO<sub>x</sub> from air is dedicated to enhancing NO adsorption by adding adsorbing components comprising of oxides of ruthenium or cerium and specific metals (Ag, Cu and Mn), all supported on titanium dioxide [113]. It is quite interesting that although the patent application was submitted in 1995, quite a few years after the birth of photocatalysis, the patent refers to the invention as a means only for promoting adsorption, without mentioning photocatalysis at all.

The A&S approach discusses in the indoor air treatment section was applied also on cementitious substrates, where a 2003 patent disclosed the use of a layer containing both TiO<sub>2</sub> and active carbon [114]. A patent on ceramic porcelain tiles for outdoor decontamination of air disclosed a variety of means to improve performance [115]. To increase NO<sub>x</sub> adsorption and absorption, zeolites or petalite were added to the photocatalytic glaze layer that contained 25% TiO<sub>2</sub>, while megalite was added to the engobe layer. Micro channels in the covering layer ensured high permeability to NO<sub>x</sub> as well as to rain drops that supposedly act to wash the formed nitrate, and likewise micro uneven areas in the thickness of the glaze were made to increase the surface area.

#### 4.1.3. Deactivation of the photocatalyst

Analyzing the patents on outdoor air treatment reveals that the main concern seems to be the removal of nitrates. Nevertheless, this seems to be an easy problem to solve, since nitrates can be easily washed away by rain. It is for this reason that high water permeability (as high as >0.01 cm/s) was mentioned as a virtue in a patent disclosing self-locking composite blocks covered with a surface layer of cementitious material containing titanium dioxide [116].

Phosphates may exhibit a more severe problem as they tend to adsorb strongly on the surface of the photocatalyst. Nevertheless, for most cases their concentration is quite small. Another source for deactivation could be aromatic compounds, as the aromatic ring tends to stay on the surface thus poisoning the catalyst. Unfortunately, we are not aware of any patents aimed at handling this issue.

#### 4.1.4. Optimizing the utilization of photons

Outdoor air treatment is characterized by the use of solar light. In that sense, the recently developed visible light photocatalysts (see Section 3.1.7) seem to be most appropriate for outdoor treatment of air.

Unlike indoor air treatment devices, where UV light is available 24 h a day (or at will), solar light is restricted to several hours a day. One way to overcome this problem is to utilize the A&S approach, such that the contaminants will be adsorbed 24 h a day and will be decomposed, whenever there is sufficient light.

#### 4.1.5. Adhesion of photocatalyst to substrates

The form by which the photocatalyst should be incorporated into the cementitious material was the subject of quite a few patents. In the first patents [117,118], assigned to Mitsubishi Materials Corporation, the photocatalyst was simply mixed together with the cement. The process was simple nevertheless the product could not be expected to have good performance since most of the photocatalytic particles were ineffective being embedded in

the bulk. Moreover, introducing high percentage of titanium dioxide could damage the mechanical properties of the cement. It is for this reason that more advanced patents leave the mechanical properties demands for a regular hydraulic cement (Portland cement) or to an aluminate cement but add a photocatalytic cementitious layer on top. This layer may contain high percentage of titanium dioxide (usually 2–10% by mass, depending on patent), together with cement and binders that provide the required adherence.

One of the relevant patents [119] disclosed the preparation of roof tiles consisting of a two layered structure where the outer layer consisted of  $\text{TiO}_2$  granules, several mm in size, that were attached to the bottom layer by a binder, that, according to the patent, could be either organic or inorganic (alkali metal silicate and phosphatic cement). To increase the active surface it was proposed to etch the surface by acids, sand blasting, or even dry-ice blasting.

The application of titanium dioxide particles to a surface is not trivial. Care has to be made that the binder will not coat the photocatalyst particle completely thus preventing its activity. Furthermore, organic binders are prone to photocatalytic degradation. Still, some patents use organic additives, with [120] or without inorganic binders. Among the organic additives one finds polyester resins [121], polycarboxylic agents, cellulosic ethers [122], polyurethane, phenol formaldehyde, cellulose nitrate [119], methyl silicate, poly(meth)acrylic acid and polytetrafluoroethylene graft-polymerized with sulfonic acid [123,124]. It is noteworthy that most patents do not address the problem of photocatalytic degradation of the organic constituents. Nevertheless, some patents claim to prevent the deterioration of the resin [125]. It is noteworthy that in many cases the organic compounds serve not as binders but rather to control the rheological properties during application [122]. From this point of view, once the photocatalytic layer is applied, their photocatalytic degradation over time can sometimes be tolerated.

Roads are required to withstand high shear rates. In order to increase the durability of the photocatalytic layer against shear, it was proposed to add an intermediate layer between the bituminous underlayer and the superficial cementitious photocatalytic top layer. One patent disclosed the use of a fiberglass reinforcement net as part of the interface layer [126], whereas a different patent, assigned to Italcementi Ltd., suggested a layer comprised of a stainless steel net connected to both layers by an epoxy resin (alternatively by polyurethane) [127]. Another option to keep the mechanical properties of roads while having a well-adhered photocatalytic layer is to prepare a bituminous base layer (10–60 mm in thickness), made of relatively large aggregates that form voids. The voids are filled, in a subsequent step, by a cement mortar that contains photocatalytic particles (2–5% by weight in the mortar), a plasticizer to fluidify the mortar (1–4% by weight of melamine resin) and amorphous silicon oxide particles (5–15% by weight) [128]. Another patent that applies the photocatalyst to voids in the cementitious substrate disclosed the use of spraying a dilute mixture made of photocatalyst and cement onto pavements, followed by rubbing [129].

For applications that do not require withstanding high levels of stress it is possible to use extrusion. The first patents described blocks made by extrusion, that, following production, were coated with an upper photocatalytic layer [130,116]. Later, a one-step extrusion process was disclosed, producing a compact material, with low water permeability, yet with sufficient photocatalytic activity for  $\text{NO}_x$  elimination, especially suitable for making roof tiles [131]. The oxygen permeability in the extruded material was controlled in the above-mentioned patent by maintaining the extrusion pressure below 50 bar, and optimizing the ratio between water to cement and the grain size distribution of the aggregates.

The average size of the  $\text{TiO}_2$  particles and their size-distribution seem to have an important effect of the efficiency of the photo-

catalyst. Several patents claimed that cementitious materials containing titanium dioxide with bimodal size distribution should be preferred [132,133]. Here, best performance was obtained by comprising two types of particles where the specific surface area of one component is five times larger than the specific surface area of the second component.

Thin coatings are adequate for transforming existing construction objects into photocatalytic. As mentioned above, the coatings can be made either from transparent, nanoparticles of titanium dioxide, or from a white paint-like solution containing larger particles, together with binders (organic, inorganic or metal-organic), and fluidizing agents.

Application of sol-gel made  $\text{TiO}_2$  nanoparticles directly on the surface, for example, by spraying, without any heat treatment is possible, as the nanoparticles tend to stick to the surface electrostatically. Nevertheless, these layers are too thin (usually less than 50 nm, otherwise sticking becomes problematic) to absorb all photons. Certain manufacturers recommend the use of a primer to assist adherence, and in certain cases the nanoparticles are surface treated physically or chemically.

A paint which was originally disclosed for indoor use as anti-bacterial and anti-odor may work well also on exterior surfaces. This paint is comprised of titanium dioxide nanoparticles adhered to highly porous inorganic layer. This porous layer is formed following reaction between nanoparticles of calcium carbonate (applied to the surface as a first layer) and an aqueous solution containing sulfate ions applied as a second layer, thus forming thin porous layer of gypsum. The second solution contains also the titanium dioxide nanoparticles, claimed to adhere quite well to the pores [134].

## 5. Conclusion

Literature survey has shown that the number of scientific publications dedicated to photocatalytic air treatment is significantly lower than the number of scientific manuscripts dedicated to photocatalytic water treatment. Yet, this comparison is reversed when one compares the number of relevant patents. This indicates a growing interest in the implementation of photocatalysis for air treatment purposes, which surpasses that of water treatment.

This manuscript tries to analyze the various patents in the area of air treatment, while differentiating between indoor air treatment and outdoor air treatment. It was assumed that patents, as such, present (or rather are supposed to present) new ways to overcome existing obstacles, on way to implementation. Specific efforts were made to characterize the main challenges and achievements en-route for successful implementation, which were categorized according to mass transport, adsorption of contaminants, quantum efficiency, deactivation, and, no less important, the adherence and the long term stability of the photocatalyst.

Commercialization of outdoor air treatment is currently by far less developed than commercialization of indoor air treatment. While this lack of commercial interest of the end-consumers seems prohibitive at present, it can still be changed in future once fundamental technological obstacles are solved and the awareness among legislators and administrators is increased.

## Acknowledgment

The assistance of Dr. Nurit Shaham-Waldman and Ms. Osnat Harrari in preparing the manuscript is gratefully acknowledged.

## References

- [1] A.E. Jacobsen, Ind. Eng. Chem. 41 (1949) 523–526.
- [2] C.F. Goodeve, J.A. Kitchener, Trans. Faraday Soc. 34 (1938) 570–579.

- [3] S. Kato, F. Mashio, *Kogyo Kagaku Zasshi* 67 (1964) 1136–1140.
- [4] V.N. Filimonov, *Dokl. Akad. Nauk SSSR* 154 (1964) 922–925.
- [5] A. Fujishima, K. Honda, *Nature* 238 (1972) 37–38.
- [6] E. Pelizzetti, M. Visca, E. Borgarello, E. Pramauro, *A. Palmas, Chim. Ind.* 63 (1981) 805–809.
- [7] J. Cunningham, J.P.J. Tobin, P. Meriaudeau, *Surf. Sci.* 108 (1981) L465–L469.
- [8] A. Mills, S.K. Lee, *J. Photochem. Photobiol. A: Chem.* 152 (2002) 233–247.
- [9] US Patent No. 6,179,972, Two stage process and apparatus for photocatalytic and catalytic conversion of contaminants, 2001.
- [10] Y. Paz, in: H.I. de-Lasa, B.S. Rosales (Eds.), *Advances in Chemical Engineering*, vol. 36, Elsevier, 2009, pp. 289–336.
- [11] Japanese Patent No. JP 51083092, Decomposition of water by light, 1976.
- [12] US Patent No. US4011149, Photoelectrolysis of water by solar radiation, 1977.
- [13] German Patent No. DE 2045562, Photocatalytic oxidation of hydrocarbons, 1971.
- [14] French Patent No. FR 2116640, Photocatalytic oxidation of isobutane, 1972.
- [15] US Patent No. US77-812478, Photoreduction of nitrogen, 1978.
- [16] US Patent No. US4303486, Photocatalytic decarboxylation of saturated carboxylic acid, 1981.
- [17] German Patent No. DE 2729760, Photooxidation of wastewaters loaded with organic material, 1979.
- [18] Japanese Patent No. JP 83-224413, Water purification, 1985.
- [19] Japanese Patent No. JP 60187322 A 19850924, Photodecomposition of wastes, 1985.
- [20] Japanese Patent No. JP 01288322 A 19880513, Deodorization by using photocatalysts, 1989.
- [21] Japanese Patent No. JP 01288635 A 19890831, Deodorants and their manufacture, method and apparatus for deodorization, and refrigerators and air conditioners using the deodorizing apparatus, 1989.
- [22] Japanese Patent No. JP 02107338, Catalyst for decomposition of polluted gas and its application, 1990.
- [23] PCT International Application No. WO9104094 A1 19910404, Gas–solid photocatalytic oxidation of environmental pollutants, 1991.
- [24] International Patent No. WO 9411092, Air treating method using photocatalyst under interior illumination, 1994.
- [25] Japanese Patent No. JP 07284634 A 19951031, Apparatus for removing air pollutants by adsorption using photocatalyst, 1995.
- [26] T.N. Obee, R.T. Brown, *Environ. Sci. Technol.* 29 (1995) 1223–1231.
- [27] US Patent No. 5,564,065, Carbon monoxide air-filter, 1996.
- [28] A.G. Agrios, P. Pichat, *J. Appl. Electrochem.* 35 (2005) 655–663.
- [29] International Patent Publication No. WO 2006/112605, Filter assembly for air purifier, 2006.
- [30] A. Fujishima, X. Zhang, C. R. Chim. 9 (2006) 750–760.
- [31] US Patent Publication No. US2005/0129591 A1, Bifunctional layered photocatalyst/thermocatalyst for improving indoor air quality, 2005.
- [32] European Patent Publication No. EP0798143 A1, Method and apparatus for purifying air including adsorbent reactivation, 1997.
- [33] European Patent Publication No. EP0769322 A1, Method of cleaning gases with a photocatalyst, 1997.
- [34] International Patent Publication No. WO 2007/076134 A2, Photocatalytic fluidized bed purifier, 2007.
- [35] US Patent No. 5,449,443, Photocatalytic reactor with flexible supports, 1995.
- [36] US Patent Publication No. US2007/0245702 A1, Honeycomb structure and manufacturing method thereof, and air cleaner and water purifier containing the honeycomb structure, 2007.
- [37] US Patent Publication No. US2005/0275118 A1, Fan apparatus with atmosphere treatment function and system thereof, 2005.
- [38] International Patent Publication No. WO 2008/119762 A1, Blowing apparatus utilizing photo-catalyst, 2008.
- [39] US Patent No. 5,604,339, Method of Photocatalytic destruction of harmful volatile compounds at emitting surfaces, 1997.
- [40] US Patent Publication No. US2006/260283, Multi-function peripheral device with air cleaning function, 2006.
- [41] US Patent Publication No. US2004/0241726 A1, Tungsten oxide/titanium dioxide photocatalyst for improving inddor air quality, 2004.
- [42] Y. Paz, C. R. Chim. 9 (2006) 774–787.
- [43] US Patent No. 4,954,465, Apparatus for removing stink, 1990.
- [44] US Patent Publication No. US2007/0264467 A1, Photocatalyst synthesized fiber product, 2007.
- [45] US Patent Publication No. US2009/0175757 A1, Titanium dioxide, single-walled carbon nanotube composites, 2009.
- [46] US Patent Publication No. US2006/0153747, Gas treatment adsorption–oxidation system, 2006.
- [47] US Patent Publication No. US2009/0098014, Structure and method of Air-purification, 2009.
- [48] US Patent Publication No. US2004/0258581 A1, Bifunctional manganese oxide/titanium dioxide photocatalyst/thermocatalyst for improving indoor air quality, 2004.
- [49] M.R. Nimlos, W.A. Jacoby, D.M. Blake, T.A. Milne, *Environ. Sci. Technol.* 27 (1993) 732–740.
- [50] US Patent No. 6464951 B1, Method, catalyst, and photocatalyst for the destruction of phosgene, 2002.
- [51] European Patent Publication No. EP0987048 A1, Catalytic process for the decomposition of organic pollutants, 2000.
- [52] US Patent No. 6,179,972 B1, Two stage process and apparatus for photocatalytic and catalytic conversion of contaminants, 2001.
- [53] International Patent Publication No. WO 2004/112958, Air purification system comprising gold/titanium dioxide photocatalyst, 2004.
- [54] W.A. Jacoby, M.R. Nimlos, D.M. Blake, R.D. Noble, C.A. Koval, *Environ. Sci. Technol.* 28 (1994) 1661–1668.
- [55] US Patent Publication No. US2004/0241040 A1, Tungsten oxide/titanium dioxide photocatalyst for improving indoor air quality, 2004.
- [56] US Patent 7255831 B2, Tungsten oxide/titanium dioxide photocatalyst for improving indoor air quality, 2007.
- [57] International Patent Publication No. WO2008/147359, Deactivation resistant photocatalyst and method of preparation, 2008.
- [58] International Patent Publication No. WO2007/136363, Siloxane resistant ultra violet photocatalysts, 2007.
- [59] International Patent Publication No. WO2007/143013, Preparation and manufacture of an overlayer for deactivation resistant photocatalysts, 2007.
- [60] US Patent Application US2006/0127288, Photocatalyst protection, 2006.
- [61] International Patent Publication No. WO2009/091367, Filters for removal of volatile siloxanes and lifetime extension of photocatalytic devices, 2009.
- [62] International Patent Publication No. WO/2007/143042, Deactivation resistant photocatalysts, 2007.
- [63] European Patent Publication No: EP0937398 A1, antibacterial and deodorant material and method for producing the same, 1999.
- [64] J.L. Falconer, K.A. Magrini-Bair, *J. Catal.* 179 (1998) 171–178.
- [65] Japanese Patent No. 2000-070673, Antibacterial deodorizing photocatalyst type filter and its production, 2000.
- [66] US Patent Publication No. US2003/0050196, Photocatalyst compositions and methods for making the same, 2003.
- [67] Japanese Patent No. 2000-107270, Antimicrobial and deodorant filter.
- [68] International Patent Publication No. WO 97/40937, In situ method for metalizing a semiconductor catalyst, 1997.
- [69] US Patent Publication No. US2009/0162567, Method for manufacturing high performance photocatalytic filter, 2009.
- [70] B. Kraeutler, A.J. Bard, *J. Am. Chem. Soc.* 100 (1978) 4317–4318.
- [71] US Patent No. 4264421, Photocatalytic methods for metalized powders, 1980.
- [72] European Patent No. EP1859850 A1, Metal-supported photocatalyst and method for preparing the same, 2007.
- [73] European Patent No. EP0826531 A2, Air-purifying filter and air-purifier for automobile, 1998.
- [74] US Patent Application Publication No. US2007/0251812 A1, Photocatalytic air treatment system and method, 2007.
- [75] European Patent No. EP1178011 B1, Titanium oxide production process, 2006.
- [76] European Patent No. EP1254863 A1, Material responsive to visible light and process for producing the same, 2002.
- [77] US Patent No. 7,615,512 B2, Titanium dioxide photocatalyst containing carbon and method for its production, 2009.
- [78] (a) European Patent No. EP1205244 A1, Photocatalytic material, photocatalytic article, method for their preparation, 2002.;  
(b) European Patent No. EP1205245 A1, Photocatalytic material, photocatalytic article, 2002.
- [79] US Patent Publication No. 2005/0226761 A1, Titanium dioxide photocatalyst containing carbon and method for its production, 2005.
- [80] International Patent Publication No. WO 2008/009919, Metal oxynitride, 2008.
- [81] US Patent application No. 2006/0124442, Device capable of removing contaminants from a fluid, 2006.
- [82] US Patent No. 6245988 B1, Metal complex photosensitizer and photovoltaic cell, 2001.
- [83] US Patent Publication No. US2003/0232186 A1, Photocatalyst coating, 2003.
- [84] US Patent Publication No. US2003/0150708 A1, Air treatment apparatus, 2003.
- [85] US Patent Publication No. US2004/0232819 A1, Illuminator capable of cleaning air, 2004.
- [86] US Patent Publication No. US2004/0226813 A1, Fluorescent lamp device capable of cleaning air, 2004.
- [87] US Patent Publication No. US2005/0244309 A1, Air cleaner with photocatalyst materials adopted for light-gauge steel frame, 2005.
- [88] R.E. Marinangeli, D.F. Ollis, *AIChE J.* 23 (1977) 415–426.
- [89] US Patent No. 5,875,384, TiO<sub>2</sub>-coated fiber optic cable reactor, 1999.
- [90] US Patent No. 5,919,422, Titanium dioxide Photo-catalyzer, 1999.
- [91] US Patent Publication No. US2008/0308405 A1, Optical fiber photocatalytic reactor and process for the decomposition of nitrogen oxide using said reactor, 2008.
- [92] US Patent Publication No. US2009/049985, Air purification system, method for purifying air inside a structure, 2009.
- [93] US Patent No. 6,752,957, Photocatalytic reactor and method for destruction of organic air-borne pollutants, 2004.
- [94] (a) European Patent No. EP0844985 A1, Self-cleaning glass and method of making thereof, 1998.;  
(b) International PCT Application No. WO9707069, Manufacture of self-cleaning glass, and the glass obtained, 1997.
- [95] PCT International Application No. WO 9841480 A1, Photocatalytically activated self-cleaning coating on substrates, especially glass, and method for their formation, 1998.
- [96] US Patent Publication No. 2007/0149393, Nano photocatalytic sol and application thereof, 2007.

- [97] PCT International Application No. WO 2000006300 A1, Method for producing high-performance material having photocatalytic function and device therefore, 2000.
- [98] US Patent Publication No. US2002/0094298, Air purifier, 2002.
- [99] International Patent Publication No. WO 95/11751, Photocatalyst binder compositions, 1995.
- [100] US Patent Publication No. US2004/0081834 A1, Thermoset resin laminated wood, 2004.
- [101] International Patent Publication No. WO 2006/008434, A novel TiO<sub>2</sub> material and the coating methods thereof, 2006.
- [102] International Patent Publication No. WO2008/144519 A1, System and method for photocatalytic oxidation air filtration using a substrate with a photocatalyst particles powder coated thereon, 2008.
- [103] US Patent Application No. US2006/0008589, Method of coating a photocatalyst on a surface of a coated substrate, 2006.
- [104] US Patent No. US2003/0180200 A1, Combined particle filter and purifier, 2003.
- [105] US Patent Publication No. 2005/0112039 A1, Ultraviolet purification system, 2005.
- [106] US Patent Publication No. US2008/0112844, Photocatalytic air purifying device, 2008.
- [107] US Patent Publication No. US2003/0019738 A1, Modular photocatalytic air purifier, 2003.
- [108] US Patent Publication No. US2009/0056539 A1, Air purifying device, 2009.
- [109] US Patent Publication No. US2004/0081596 A1, Device case and air purifier arrangement, 2004.
- [110] US Patent Publication No. US2009/0010801, Air cleaner, 2009.
- [111] Y. Murata, H. Tawara, H. Obata, K. Takeuchi, *J. Adv. Oxid. Technol.* 4 (1999) 227–230.
- [112] A. Strini, S. Cassese, L. Schiavi, *Appl. Catal. B: Environ.* 61 (2005) 90–97.
- [113] European Patent Publication No. EP0722763 A1, NO<sub>x</sub> adsorbents, 1996.
- [114] Japanese Patent No. JP 2003026485, Ligneous cement plate provided with chemical substance-adsorbing and decomposing layer, 2003.
- [115] International Patent Publication No. WO 2004/094341 A1, A procedure for the realization of ceramic manufactures, in particular porcelain stoneware tiles and trim pieces, with anti-pollution and anti-bacterial properties and products thereby obtained, 2004.
- [116] US Patent Publication No. 5861205, NO<sub>x</sub> cleaning paving block, 1999.
- [117] Japanese Patent No. JP 10043549, Manufacture of materials for NO<sub>x</sub> removal, 1998.
- [118] Japanese Patent No. JP 200117117, Photocatalyst material, 2000.
- [119] UK Patent Publication No. GB 2425075 A, Concrete roof tile or wall cladding element, 2006.
- [120] US Patent Publication No. US2007/167551, Coating composition having surface depolluting properties, 2007.
- [121] European Patent No. EP1834935, Wall and floor tiles and slabs made of agglomerated stone in polyester matrix with TiO<sub>2</sub> photocatalyst added for self-cleaning and antibacterial activity, 2007.
- [122] International Patent No. WO/2009/013337, Coatings based on hydraulic binders with an optimal rheology and high photocatalytic activity, 2009.
- [123] Canadian Patent No. 2640908 A1, Coating material; building material and method for coating building material, 2008.
- [124] US Patent Application No. 2009/0142604, Coating film for building material, 2009.
- [125] Japanese Patent No. JP 2002191984, Photocatalyst compositions, thermoplastic resin compositions and articles containing same photocatalyst compositions, 2002.
- [126] European Patent No. EP1609910, A pavement with photocatalytic effect, 2005.
- [127] International Patent No. WO/2006/000565, High durability photocatalytic paving for reducing urban polluting agents, 2006.
- [128] European Patent No. EP1752429 A1, Bituminous road surface with a photocatalytic effect and a procedure for the preparation of said road surface, 2007.
- [129] Japanese Patent No. JP 2002242113, Coating method of photocatalyst layer to pavement for air purification, 2002.
- [130] Japanese Patent No. JP 10219920, Extrusion-molded building materials for removal of nitrogen oxide and their manufacture, 1998.
- [131] International Patent No. WO/2008/017934, New precast cementitious products with photocatalytic activity, 2008.
- [132] US Patent Publication No. US2008/0236450, Photocatalytic granular mixture for mortar and concrete and its use, 2008.
- [133] International Patent No. WO/2004/074202, Cement-based paving blocks for photocatalytic paving for the abatement of urban pollutants, 2004.
- [134] International Patent No. WO/2009/074120, Multifunctional photocatalytic and sanitary paints and the method of application thereof, 2009.